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EXAMINATION OF THE COMPLETE OIL BREAKDOWN RATE ANALYZER MODEL 2 (COBRA 2) AND THE TANDEM CONDUCTIVITY TESTER (TCT) FOR DETECTING SYNTHETIC AIRCRAFT OIL DEGRADATION

Edward Todd Urbansky, Ph.D.
Chemist, YD-02, United States Air Force
Special Projects Department Head, JOAP TSC

Denedra Brown
Staff Sergeant, United States Army
Logistics Department, JOAP TSC

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JOAP TSC

JOINT OIL ANALYSIS PROGRAM
TECHNICAL SUPPORT CENTER
85 Millington Avenue
Pensacola NAS, FL 32508-5020

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14. ABSTRACT

At the request of the U.S. Air Force Oil Analysis Program (AF OAP) Office, two commercial products were evaluated for applicability to the analysis of synthetic ester (polyol) aircraft lubricant with a base stock of 1,1,1-(trimethylol)propane triheptanoate (TMPTH): the Complete Oil Breakdown Rate Analyzer (COBRA 2) and the Tandem Conductivity Tester from Spectro, Inc. The two units were examined by running a series of conductivity standards of tricresyl phosphate (TCP) in TMPTH. Because no aircraft oil samples were available at the time of testing, marine diesel engine oil samples were used to investigate the impacts of worst-case contaminants found in engine oil. The COBRA 1 tester provided the benchmark for comparison/contrast. This study was of limited scope, using a single instrument of each model for testing; however, no major problems or differences were identified based on available samples. Precision and accuracy were similar to the COBRA 1; nevertheless, some confounding factors were observed with the TCT, especially regarding differences among measurement boats. Both instruments met minimal performance standards for consideration of adoption by the joint military services within the scope of the AF OAP needs. Recommendations are made for the improvement of the devices as well as for standardization and optimization of performance should either unit be adopted.

15. SUBJECT TERMS

oil analysis, burnt oil, black oil, F100, COBRA, Complete Oil Breakdown Rate Analyzer, TCT, Tandem Conductivity, polyol oil, ester oil, trimethylolpropane triheptanoate, aircraft oil, lubrication, lubricity, degradation

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Report Authors:	Edward Todd Urbansky, Ph.D., YD-02, USAF Denedra Brown, SSG, USA
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This report has been reviewed and is approved for publication in accordance with the Joint Instruction designated as Air Force Instruction 21-131(I), Army Regulation 700-132, and OPNAVINST 4731.1B.

/s/

Daniel A. Jensen
Major, United States Army
Director
Joint Oil Analysis Program
Technical Support Center

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EXAMINATION OF THE COMPLETE OIL BREAKDOWN RATE ANALYZER MODEL 2 (COBRA 2) AND THE TANDEM CONDUCTIVITY TESTER (TCT) FOR DETECTING SYNTHETIC AIRCRAFT OIL DEGRADATION

EXECUTIVE SUMMARY

At the request of the U.S. Air Force Oil Analysis Program (AF OAP) Office, two commercial products were evaluated for applicability to the analysis of synthetic ester (polyol) aircraft lubricant with a base stock of 1,1,1-(trimethylol)propane triheptanoate (TMPTH): the Complete Oil Breakdown Rate Analyzer (COBRA 2) and the Tandem Conductivity Tester from Spectro, Inc. The two units were examined by running a series of conductivity standards of tricresyl phosphate (TCP) in TMPTH. Because no aircraft oil samples were available at the time of testing, marine diesel engine oil samples were used to investigate the impacts of worst-case contaminants found in engine oil. The COBRA 1 tester provided the benchmark for comparison/contrast. This study was of limited scope, using a single instrument of each model for testing; however, no major problems or differences were identified based on available samples. Precision and accuracy were similar to the COBRA 1; nevertheless, some confounding factors were observed with the TCT, especially regarding differences among measurement boats. Both instruments met minimal performance standards for consideration of adoption by the joint military services within the scope of the AF OAP needs. Recommendations are made for the improvement of the devices as well as for standardization and optimization of performance should either unit be adopted.

Edward Todd Urbansky, Ph.D., YD-02, USAF ■ Denedra Brown, SSG, USA
JOAP Technical Support Center ■ 85 Millington Avenue ■ Pensacola NAS, FL 32508
Phone: 850-452-5627 ■ Voice DSN: 922-5627 ■ Fax: 850-452-2348 ■ Fax DSN: 922-2348

1. Introduction

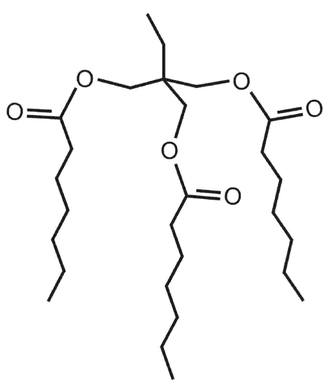
1.1. Background

Synthetic aircraft oil is known to undergo breakdown during both normal use and abnormal stress (*1, 2*). The complete oil breakdown rate analysis (COBRA) is based on the conductivity of the oil that results from the chemical functionalization (oxygenate formation/partial combustion and thermal degradation/pyrolysis) of the oil. This phenomenon is observable through its burnt/acrid odor, darkening, and some visible soot production as well as increases in viscosity and acidity.

The base stock for synthetic oil is produced via the complete reaction between 1,1,1-(trimethylol)propane, **1**, and heptanoic acid, **2**, to give the ester 1,1,1-(trimethylol)propane triheptanoate (TMPTH), **3**. Most synthetic aircraft engine oils also contain antiwear ingredients. Tritolyl phosphate is the most common, **4**; within the lubricant industry, the synonym tricresyl phosphate (TCP) is more commonly used. The tolyl group may be present as any geometric isomer or a mixture, even within the same molecule. For this reason, the placement of the methyl group is represented as indeterminate in **4**. The *ortho* isomer is classified as a severe marine pollutant by the U.S. Department of Transportation. Formulations containing less than 1% w/w of *ortho* isomer are classified as marine pollutants, while those containing 1% w/w or more are classified as severe marine pollutants (49 CFR 172).

$CH_3CH_2C(CH_2OH)_3$
1

$CH_3(CH_2)_5CO_2H$
2



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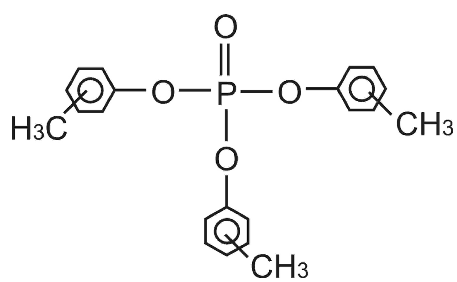

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In addition to the regular degradation products, TMPTH and TCP can also react to give, for example, trimethylolpropane phosphate (*3*); these reaction products also affect conductivity. All of these species will be referred to as degradates here, regardless of the process that forms them. Degradation processes occur during normal use, but their rates can be increased as a result of poor engine performance. The build-up of degradates eventually lowers oil performance until it adversely affects engine health and increases wear. For certain aircraft and/or engines, this has been especially problematic, while most have had no issues. In general, aircraft oil undergoes minimal testing because so much of it is consumed during normal use. That notwithstanding, the unconsumed oil

Figure 1.1. The COBRA II instrument is produced by NAECO, LLC. The top knob is the zero (intercept/offset); the middle knob is the calibration (slope). The *on* button (bottom left) is depressed to measure. The LCD display in the center shows an integer signal. The conductance/conductivity cell at the right is held partly open in the photograph.

remains in the aircraft with little knowledge of its overall quality. Much like fuel, aircraft oil that has been placed into equipment is primarily monitored in terms of quantity rather than quality.

Some additional history is helpful at this point. The original analog COBRA unit was first fielded in the 1980s (*2*). An in-flight COBRA sensor, laboratory/field model, viscosity, and total acid number (TAN) measurement were all examined. The COBRA was selected primarily on account of its cost, durability, ease-of-use, and portability when contrasted with TAN titrimetry and viscometry (*2, 4*). The lab/field COBRA unit was found to be reliable and was generally correlated with viscosity and TAN. By the mid-1980s, the COBRA units were decomissioned when engine design changes eliminated their usefulness. In the 1990s, problems with the F100 engine eventually led to re-establishment of an updated COBRA I unit with a digital display. Initially, the AF had relied substantially on sight and smell tests by field personnel, but these proved to be too subjective and unreliable (*2*). A problem was identified with a resistor in the COBRA I unit that led to drift during extended measurements; the insertion of a diode helped to reduce this drift problem. The new instrument was named COBRA II (Figure 1.1), although COBRA I units without the diode remain in service today. The original vendor of the COBRA I and II discontinued business, leaving the AF without a supplier. The COBRA II design was reverse-engineered from existing models, and new units (COBRA 2 hereafter) were manufactured and offered for sale to the government.

Figure 1.2. Spectro TCT boat is made from PVC and has a conductivity cell on a G10 plate. The plate forms the boat bottom. Electrical conductors pass through the PVC to contacts outside the boat. © Spectro, Inc.; used with permission.

1.2. Available Technology and Its Application

Although not part of the testing or evaluation process for the instruments, proper use is supported by proper limits with due regard for experimental error. Previous reports have recommended limits of 10 (*2*) and 12 (*5*). At present, the F100 decision guide in the JOAP Manual gives this guidance: COBRA signal change must not exceed 3 units per 10 operating hours or per flight, (ii) abnormal range is 10 or higher (*6*). This type of guidance must be factored into any evaluation of the instrumentation because it goes directly to the data use objectives with their concomitant data quality requirements.

More recently, the Tandem Conductivity Tester (TCT) offered by Spectro, Inc., joined the technologies available for oil quality assessment. The TCT is a modular feature that can be incorporated into the existing Spectroil M/N rotrode atomic emission spectrometers already widely in use, especially in the AF OAP. The TCT adaption requires three parts: (i) a retrofitted boat holder with supporting electronics and wiring for interface to the system, (ii) supporting

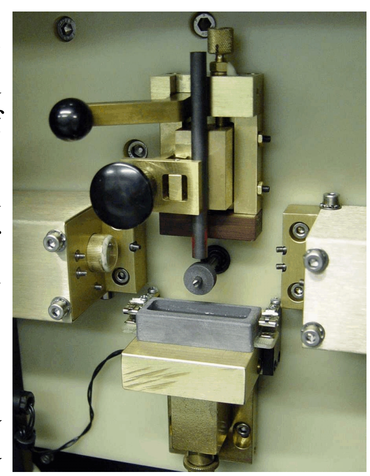

Figure 1.3. Spectrometer chamber is shown retrofitted with new boat holder and TCT boat. Electrical contacts press on each side of the G10 plate. © Spectro, Inc.; used with permission.

software, and (iii) a set of semiconsumable polyvinylchloride (PVC) boats. Each boat has a conductivity cell on a G10 plate that is inserted through the boat and epoxied into place (Figure 1.2). The G10 bottom extends from each side of the boat so that the conductors are exposed on the upper surface. The retrofitted boat holder (Figure 1.3) has contacts that hold the boat in place and touch the conductors on the boat. Both the COBRA and the TCT read an arbitrary unit related to conductivity and related to a measured conductance (resistance) by a fixed cell. An early TCT and Fourier transform infrared (FTIR) spectrometry were evaluated by the JOAP TSC in 1997 (*5*). Over the region of interest (COBRA signal $\leq$ 12) performance of the COBRA II, an FTIR spectrometric method, and the TCT were commensurate with one another. The authors recommended that the TCT be considered for adoption and felt factors other than data quality would influence the choice of technology for the determination of degraded oil. In fact, cost was and continues to be the major factor in selecting the COBRA II over the TCT. That notwithstanding, the manufacturing cost of the TCT has fallen to the point where it competes favorably.

By 1997, 50 COBRA II instruments had been purchased. Accordingly, the USAF has a considerable infrastructure investment already. Nonetheless, additional site needs and normal depreciative loss (replacement) lead to periodic, but ongoing, procurement.

1.3. Aim of Investigation

The Air Force Oil Analysis Program (AF OAP) Office at Tinker AFB (Oklahoma City) is responsible for the selection and procurement of devices for field/lab testing of synthetic aircraft oil. At present, two items are offered for sale for this purpose. The first item is the COBRA 2, which is described above. The reverse-engineered COBRA 2 has not been tested by the JOAP TSC before. The second item is the TCT. At the request of the AF OAP Office, the JOAP TSC examined a COBRA 2 unit and a TCT unit, using the COBRA I (hereafter COBRA 1) as a baseline for performance.

2. Experimental Section

2.1. Equipment Calibration

COBRA 1 and COBRA 2 instruments were set with a JOAP TCP COBRA standard prepared to read 8. The tandem conductivity tester (TCT) was installed by Spectro, Inc., staff into a Spectroil M/N. The TCT was calibrated with the same COBRA standard. The TCT was designed to accept only a two-point external calibration: a blank with a signal of 0 and a nonzero standard with a signal of 6 or 8 normally. A set of 18 TCT boats was provided for this study. The instrument was reconfigured to run the TCT only and not perform routine atomic emission spectrometry.

2.2. Standards and Samples

A series of solutions were prepared with tricresylphosphate (TCP) concentration ranging from 0 to 58% w/w in trimethylolpropane triheptanoate (TMPTH). Because no synthetic aircraft oil samples were available to us at the time of the testing, a selection of marine diesel engine (MDE) oil samples was taken from the laboratory stream.

2.3. Performance Evaluation

Experiments were set up to investigate reproducibility and repeatability. Of particular interest was the performance of the same boat and the performance among multiple boats for the TCT. Sensitivity and practicability of enhanced calibration were evaluated via the TCT-in-TMPTH solutions. Correlations among the COBRA 1, COBRA 2, and TCT were included. The impact of the TCT boats on rotrode atomic emission spectrometry was not requested or assessed. The aim of the investigation was to ascertain the comparability and interchangeability of the COBRA 1, COBRA 2, and TCT.

3. Analysis, Results, and Discussion

3.1. Agreement, Sensitivity, and Precision

Arithmetic mean values for quintuplicate measurements on a series of 15 TCP-in-TMPTH standards are given in Table 3.1. As Table 3.1 and Figure 3.1 indicate, the TCT signal was always below the COBRA 1 signal; this suggests a correctable bias. The COBRA 1 and COBRA 2 curves actually cross, suggesting there may be some difference between the two units. At most, the difference was around 2 units of deviation from COBRA 1. On the TCP-in-TMPTH standards, correlation of both COBRA 2 and the TCT with COBRA 1 is high with a coefficient of 0.99. Deviation is largest at low readings. Near 55.6% TCP (signals of 8-9), COBRA 2 and TCT are nearly identical. Somewhat surprisingly, both deviate low by around 2 units for the 55.6% TCP standard relative to the COBRA 1, which has a signal of 11. Whether this has any impact is debatable because a ± 2 unit difference between instruments is to be expected and there is only a two-point calibration of the units. Furthermore, only a single instrument of each type was available; therefore, the normal variation among instruments of the same model is unknown. It is unfortunate that the COBRA 2 and the TCT nearly converge near signals of 8-10, since this begins to include the abnormal range. This could possibly be improved by changing the calibration standards to 8 and 10 with readings as below 8 all lumped together (as opposed to 0 as one of the points). However, it would require some changes to the extant COBRA devices.

Correlations of both COBRA 2 and TCT with COBRA 1 on MDE oil samples are good with respective coefficients of 0.9402 and 0.9181 (Table 3.2). It is important to keep in mind that this level of performance was accomplished using one boat for all TCT testing. Despite precision machining, conductivity cells are extremely susceptible to small variation.

Table 3.1. Signals[a,b,c] for COBRA 1, COBRA 2, and TCT[d] for a series of TCP-in-TMPTH standards

TCP Concentration (mass fraction)	COBRA 1 signal	COBRA 2 signal	TCT signal
0.000	1.0 ± 0.0	2.00 ± 0.0	0.18 ± 0.06
0.077	1.0 ± 0.0	2.60 ± 0.5	0.14 ± 0.01
0.143	1.6 ± 0.5	3.00 ± 0.0	0.05 ± 0.02
0.200	2.0 ± 0.0	3.00 ± 0.0	0.38 ± 0.12
0.250	2.8 ± 0.4	4.00 ± 0.0	0.44 ± 0.07
0.294	3.0 ± 0.0	4.00 ± 0.0	1.04 ± 0.11
0.333	4.0 ± 0.0	5.00 ± 0.0	1.91 ± 0.14
0.368	5.0 ± 0.0	5.00 ± 0.0	2.83 ± 0.19
0.400	5.4 ± 0.5	5.80 ± 0.0	3.54 ± 0..23
0.429	5.8 ± 0.4	6.80 ± 0.4	4.17 ± 0.25
0.478	8.0 ± 0.0	7.20 ± 0.4	5.96 ± 0.51
0.500	8.0 ± 0.0	8.00 ± 0.0	6.74 ± 0.25
0.520	9.0 ± 0.0	8.00 ± 0.0	7.38 ± 0.29
0.538	10.2 ± 0.4	8.60 ± 0.5	8.03 ± 0.40
0.556	10.8 ± 0.4	9.00 ± 0.0	8.70 ± 0.30

Notes: (a) Reported signals are arithmetic means of quintuplicate analyses. Although all devices report whole number values, the Spectro TCT will report decimal values for the mean and estimated standard deviation when the mathematical operation is performed within the instrument control and data acquisition software. (b) The trigger level for maintenance action is taken as 10, with a performance cut-off (minimum reading) at 6 or 8 for the purpose of the two-point calibration. Consequently, large deviation from COBRA 1 benchmark reading or error becomes irrelevant below readings of approximately 5.5 (~41% w/w TCP). (c) Reported uncertainties are the estimated standard deviations, which are often zero due to rounding with COBRA units; the actual experimental error should be regarded as ± 1 unit. (d) One boat was used for all TCT analyses.

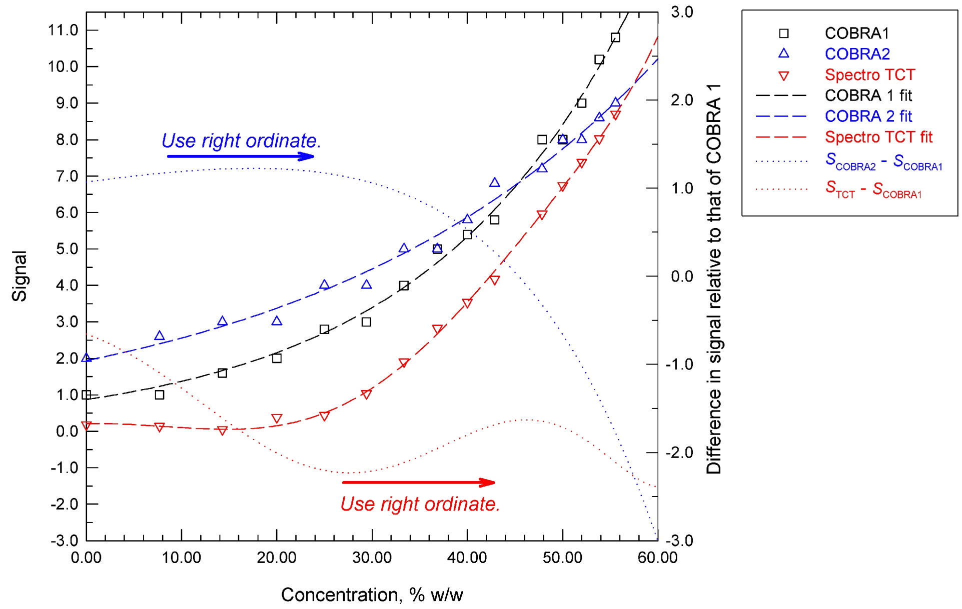

Figure 3.1. Calibration curves on the COBRA 1, COBRA 2, and TCT obtained from arithmetic means of quintuplicate measurements of TCP-in-TMPTH standards. Boat A was washed in acetone and reused for the TCT.

Table 3.2. Instrument signal[a,b] and correlation with COBRA 1 for oil samples from marine diesel engines using one TCT boat for all analyses

Sample	COBRA 1	COBRA 2	TCT
C-8[c]	7.2	7.0	5.30 ± 0.33
A	4.2	4.0	1.36 ± 0.22
B	4.0	4.0	1.82 ± 0.13
C	6.0	5.0	4.41 ± 0.48
D	6.0	5.0	6.20 ± 0.16
E	6.0	5.0	5.42 ± 0.53
F	2.0	3.0	0.33 ± 0.05
G	4.0	4.0	2.02 ± 0.15
H	2.0	3.0	0.95 ± 0.08
I	4.2	4.0	3.43 ± 0.21
J	5.0	4.0	3.34 ± 0.33
K	2.0	3.0	0.96 ± 0.03
L	2.0	3.0	1.01 ± 0.04
r^2	unity	0.9402	0.9181

Notes: (a) Signals are arithmetic means based of five replicates. (b) COBRA units give only whole number values. Uncertainty for the COBRA data is ± 1 unit. Reported uncertainties for the TCT data are estimated standard deviations. (c) C-8 refers to a JOAP COBRA standard made to read 8.

3.2. Nonlinear calibration and curve-fitting analysis

Discussion of calibration here refers specifically to fitting the ordered pairs (x, y) to a function where x is the TCP concentration (as a decimal mass fraction, not percent) and y is the arithmetic mean of the measured signal and not the manufacturer's single-point calibration used prior to operation. Fitting was accomplished using Tablecurve2D (version 5.01), and goodness of fit parameters were computed directly by the software. Unlike the COBRA units, the TCT-equipped spectrometer provides a more precise measure of repeatability in that it reports numeric values with a large number of significant digits. This allows an estimated standard deviation to be calculated for tests conducted under repeatability conditions, such as same boat and same aliquot of sample. A number of criteria were considered in the determination of goodness of fit, including regression coefficient, degrees of freedom (DoF) adjusted regression coefficient, standard error, and maximum error.

One of the dangers of using automated curve-fitting is the overreliance on certain fit quality measures. It is necessary to guard against automated selection of those curves with excessive numbers of fitting parameters or those for which no physical rationale can be made. Certain types of functions, especially polynomial expansions of ascending order (e.g., $y = a + bx + cx^2 + \ldots$) or composite functions that incorporate such or similar expansions (e.g., $y = a + b \ln x + c (\ln x)^2 + \ldots$, $y = a + b/x + c/x^2 + \ldots$, or $1/y = a + bx + cx^2 + \ldots$), are prone to overfitting, where an excessive parameters are invoked to give a (nearly) perfect fit to the experimental data even though the overall curve shape is unjustifiable and sometimes nonsensical; this phenomenon is associated with a failure to take into account the degrees of freedom when deciding on the number of fitting parameters. For this reason, "constant sign of first derivative" or the "constant trend in first derivative" filters built into the software were typically employed. These eliminate oscillatory and many stepping/boxing functions. It is further important not to over-rely on miniscule improvements in r^2 or the standard error, even with weighted functions; an important role remains for visual inspection. Furthermore, there are cases where the data span a region that is insufficient to distinguish among competing functions. In other words, physicochemical common sense must be used to evaluate the reasonableness of the function for representing both real quantities and the specific quantity, especially for functions that exhibit significant features (critical points, inflection points, discontinuities, asymptotes, etc.) that may arise upon extrapolation outside the experimental domain or expansion of the domain via experiment.

It was found that the COBRA 1 and COBRA 2 data were best fitted to exponential functions, but reasonable fits could also be obtained with polynomial expansions. Nevertheless, the DoF- adjusted regression coefficients and the relative standard errors of the fitting parameters indicate that the exponential function is a better choice for COBRA 2. The COBRA 2 case is noteworthy in that relying on comparison of the DoF-adjusted regression coefficients correctly picks the better fit while relying on a comparison of the unadjusted coefficients yields a poorer choice, even though the difference between the two DoF-adjusted coefficients is small. The standard errors are quite large for the parameters, especially b, suggesting this is a considerably weaker fit despite the rather good fit suggested by visual inspection. Equation ③ was rejected for the COBRA 2 data because of both its unnecesary complexity and of its high standard errors for fitting parameters b, c, and d relative to their magnitude—this despite the higher DoF-adjusted r^2 relative to equation ②. Moreover, selection of the same function for both COBRA 1 and COBRA 2—two instrument models based on the same fundamental principles and very similar components—is far preferable. After all, there is no basis for arguing for a difference among instruments, but rather a strong argument in favor of similar behavior. Table 3.3 gives the data for the various fitting expressions.

Table 3.3. Calibration curve fitting for the COBRA units (models 1 and 2): equations and goodness of fit indicators[a]

Fitting function	Model[b]	Parameters	r^2	DoF adj r^2	Fit std error
① $y = \exp(a + bx)$	1*	$a = -0.138 \pm 0.064$ $b = 4.53 \pm 0.13$	0.9946	0.9937	0.2548
	2*	$a = 0.6632 \pm 0.045$ $b = 2.7673 \pm 0.096$	0.9894	0.9876	0.2507
② $y = a + bx + cx^2$	1	$a = -0.186 \pm 0.158$ $b = 4.79 \pm 0.78$ $c = -0.317 \pm 0.952$	0.9947	0.9932	0.2635
	2	$a = 2.16 \pm 0.20$ $b = 1.62 \pm 1.50$ $c = 19.2 \pm 2.4$	0.9902	0.9875	0.2510
③ $y = a + bx^2 + cx^4 + dx^6$	2	$a = 0.928 \pm 0.172$ $b = 29.3 \pm 5.8$ $c = -29.5 \pm 46.9$ $d = 125 \pm 102$	0.9953	0.9934	0.2603
④ $y = (a + bx + cx^2 + dx^3)^{-1}$	2	$a = 4.14 \pm 0.48$ $b = 35.8 \pm 10.3$ $c = -130 \pm 53$ $d = 567 \pm 70$	0.9912	0.9878	0.2474

Notes: (a) Unweighted fits were obtained using Tablecurve2D version 5.01 and were based on quintuplicate measures of 15 TCP-in-TMPTH standards (0.0-55.6% w/w); y = instrument signal; x = concentration as mass fraction (decimal not percent). (b) The asterisk (*) next to the model number indicates the function selected for fitting the data, constructing Figure 3.1, and discussing performance.

On the other hand, the Spectro TCT data were best fitted to a polynomial expansion; the various fits are given in Table 3.4. When all the data are considered, function ⑧ is the best choice and the only one that accommodates the absolute maximum present in the data while keeping the number of parameters to a reasonable level. This fit is shown in Figure 3.1.

Near the detection limit (≤ 20% w/w TCP; readings below 1), the sensitivity falls to nearly zero, and an absolute minimum occurs, but not at zero, as seen in Figure 3.1. This makes fitting the curve somewhat more challenging because there is no obvious physical justification for the minimum to occur at a concentration above zero. Fortunately, there is no need to measure accurately in this region; accordingly, this anomolous behavior is immaterial. As the TCP concentration increases over 20% w/w, the instrument response becomes well-behaved. Above 30% w/w TCP, the instrument response is readily fitted to a variety of simple functions. As Figure 3.1 shows, the difference between the fit for the TCT and that for COBRA 1 never exceeds 2.5. With rounding error, this would suggest ± 2 units, which realistically must be considered within the experimental error since COBRA 1 has an error of ± 1 unit and TCT has an error of ± 1 unit. The reliance on a two-point calibration (zero and 6 or 8) also contributes to this error. For the higher concentration data, the quadratic equation ⑤ was selected on account of its general acceptance despite the high standard errors of the parameters shown in Table 3.4. Even though equation ⑥ is preferable in terms of the standard errors of the fitting parameters and simplicity, this equation is more difficult to fit and not available in many canned data analysis software packages. Figure 3.2 shows that equations ⑤ and ⑧ are not distinguishable in terms of the goodness of fit for the TCT data where TCP concentration exceeds 20% w/w albeit only data over 30% were used to obtain the fitting parameters. It is important to realize that points from the low concentration region should be omitted from the fitting process due to the low sensitivity and low analytical interest if fits are to be used in the decision-making process.

Table 3.4. Calibration curve fitting for the TCT: equations and goodness of fit indicators[a]

Fitting function	All data[b]	Parameters	r^2	DoF adj r^2	Fit std error
⑤ $y = a + bx + cx^2$	N[c]	$a = -0.492 \pm 1.39$ $b = -6.66 \pm 6.60$ $c = 41.9 \pm 7.6$	0.9988	0.9980	0.0992
⑥ $y = a + bx^{2.5}$	N	$a = -0.667 \pm 0.078$ $b = 41.17 \pm 0.605$	0.9985	0.9980	0.1024
⑦ $y = (a + bx)^2$	N	$a = -0.930 \pm 0.095$ $b = 7.01 \pm 0.20$	0.9986	0.9981	0.0989
⑧ $y = a + bx^2 + cx^4 + dx^6 + ex^8$	Y[c]	$a = 0.217 \pm 0.015$ $b = -15.55 \pm 1.97$ $c = 398 \pm 42$ $d = -1318 \pm 276$ $e = 1555 \pm 537$	0.9980	0.9969	0.0283
⑨ $y = a + bx^{0.5} + cx + dx^{1.5} + ex^2 + fx^{2.5} + gx^3$	Y[c]	$a = 0.180 \pm 0.085$ $b = 1.21 \pm 103$ $c = -37 \pm 1144$ $d = 320 \pm 4910$ $e = -1154 \pm 10204$ $f = 1776 \pm 10305$ $g = -910 \pm 4057$	0.9955	0.9910	0.0477

Notes: (a) Unweighted fits were obtained using Tablecurve2D version 5.01 and were based on quintuplicate measures of 15 TCP-in-TMPTH standards (0.0-55.6% w/w); y = instrument signal; x = concentration as mass fraction (decimal not percent). (b) Y = Yes. N = No; data below 30% w/w TCP excluded from fit. (c) Fits based on equations ⑤ and ⑧ are shown in Figure 2. The fit to equation ⑨ has such large standard errors for the parameters that only one is statistically distinct from zero, making this function a poor choice despite its correlation coefficient.

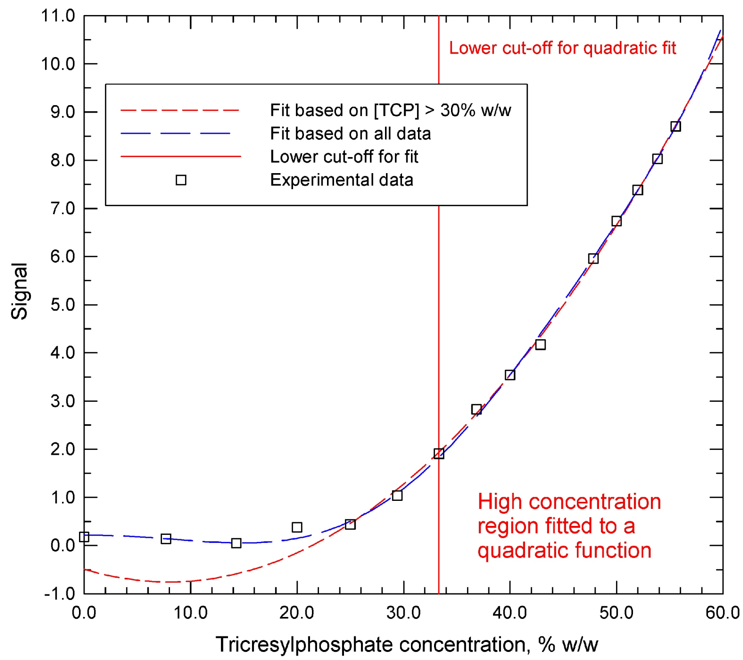

Figure 3.2. TCT calibration curve is shown: TCT data (arithmetic means from quintuplicate runs) for TCP-in-TMPTH standards. Over the region of interest, a curve fitted to only the high concentraiton data agrees well with a curve fitted to all the data, albeit the two functions are different. The detection limit is somewhere near 25% w/w TCP with a "COBRA" signal below 1. Because signal values below 1-2 have no real programmatic importance, the shape of the curve in this region and the detection limit are of minor interest.

3.3. Boat Health and Lifetime

One of the issues identified during testing was the susceptibility of the boats to certain solvents and sample types. Both high tricresyl phosphate and acetone led to a visible modification to the boats. In some cases, the change appeared to be a film or coating, but in other cases the cell material appeared to be degraded. This was not explored more fully, but was reported to the manufacturer for its consideration.

3.4. Boat-to-Boat Signal Agreement

One of the curiosities of the data taken on multiple boats (Table 3.5) is nicely illustrated by Figure 3.3. The boat designations were rearranged so that the data proceed in increasing signal order. A trend is clearly visible, and it is significant relative to the uncertainties in the individual arithmetic means (based on quintuplicates [TCP Standard, MDE oil A, and MDE oil D(5x)] except for the duplicate mean for MDE oil D [i.e., D(3x)], which was based on triplicate measurements). The trend visible in the standard (a TCP-in-TMPTH solution made to give a signal of 6) is not visible at all for the other samples. In addition, the repeat of MDE oil D does not lie on top of the first run, although there is some similarity; the correlation coefficient is a lackluster 0.283 for 10 boats (A-J). The correlations among the data paired with the TCP standard by boat are very poor, ranging from –0.5 to +0.5 for boats A-E (Table 3.5). It is possible that this stems at least partly from differences in the boats that cannot be accounted for using a two-point calibration. Regardless, it is clear that there can be up to a 3-unit deviation when changing boats. Differences among the various measures of central tendency (arithmetic/geometric means, median) are small (< 8%), suggesting that the data are reasonably uniformly distributed.

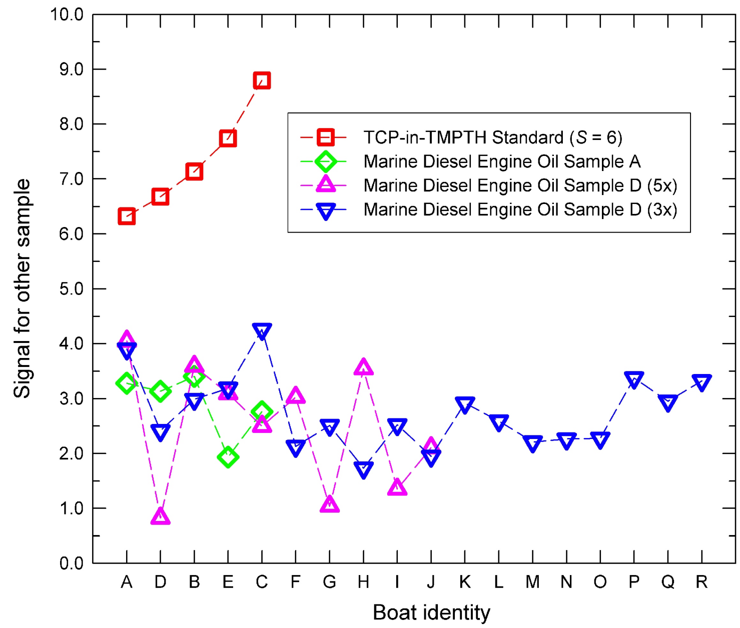

Figure 3.3. Variation is observed as the TCT boat is changed. For the TCP-in-TMPTH standards, boat order was rearranged so that the associated signals would be in ascending order. However, the other samples do not follow the trend of increasing signal typical of a correctable bias. Moreover, the repeat of MDE oil D does not follow the original trend for MDE oil D. Regardless of the lack of trend agreement, the variation in signal for the homogeneous standards as a function of boat indicates that additional standardization is required.

3.5. Artefacts of Sample Type or Subsampling

It was unfortunate that no synthetic aircraft oil samples were available during the test period. Oil samples from marine diesel engines are considerably dirtier than samples from aircraft engines. Furthermore, marine diesel engine oil is permitted to contain more metal debris than aircraft engine oil is permitted to contain. Differences in debris on the sensor may be an artefact of the laboratory sampling process. The TCT boat requires decanting considerable volume (2-3 mL) of oil from the field sample bottle, while the COBRA unit sensor requires 1-2 drops of oil drawn up on a glass rod. Therefore, large debris that would have had time to settle and that would not adhere to the glass rod may fall along the side of the bottle and be poured into the TCT boat. This may account for the high repeatability within a boat on the same aliquot of oil, but pour repeatability when the boat is washed out and a new aliquot of oil is placed into it. It may also account for the poor repeatability among the boats since each is associated with an individual aliquot of oil from the sample container. This is further supported by the high repeatability among boats on the homogeneous TCP-in-TMPTH standard. Nonetheless, this premise remains speculative due to the lack of synthetic aircraft oil samples for investigation.

Table 3.5. Summary data and results for the various TCT boats (same data as Figure 3.3)

	TCP Standard[a]		MDE Oil A[b]		MDE Oil D (5×)[b]		MDE Oil D (3×)[b]		Data[c]
Statistic	signal	esd[d]	signal	esd[d]	signal	esd[d]	signal	esd[d]	
Number of data	5	5	5	5	10	10	16	16	
Maximum	8.795	0.536	3.403	0.100	4.047	0.549	4.261	0.694	all
Minimum	6.319	0.034	1.934	0.021	0.824	0.033	1.732	0.040	all
Range	2.476	0.502	1.469	0.079	3.223	0.516	2.529	0.654	all
Arithmetic mean	7.334	0.276	2.903	0.060	2.511	0.164	2.751	0.381	all
Geometric mean	7.284	0.181	2.846	0.050	2.473	0.164	3.285		all
Median	7.136	0.303	3.133	0.067	3.091	0.191	3.190		all
Estd std dev	0.871	0.193	0.530	0.032	1.082	0.156	0.655	0.181	all
Estd std dev of the mean[e]	0.390	0.086	0.237	0.014	0.342	0.049	0.154	0.043	all
r^2 with TCP std[f]	unity		-0.533		0.057		0.525		1st 5
r^2 (D-D)[g]							0.283		1st 10

Notes: (a) TCP Standard is made to have a COBRA signal of 6. (b) MDE refers to marine diesel engine oil samples from the regular laboratory stream. MDE oil sample D was split and run in quintuplicate the first time and triplicate the second time to see if the values obtained for a given boat would be repeatable. (c) Data refers to the data used in calculating the statistics as reported. For the correlations, equal numbers of sets of data representing ordered pairs tied to a specific TCT boat were used, and the additional data were ignored. (d) The esd columns refer to the estimated standard deviations obtained for individual runs. For example, 0.549 (row 1, column 7) was the largest esd obtained out of 10 boats tested 5 times each of MDE oil sample D. (e) Estimated standard deviation of the mean is an estimate of uncertainty for the arithmetic mean = $s/n^{1/2}$, where s is the estimated standard deviation and n is the number of data. (f) Correlation with the TCP standard is poor; the upward trend shown for the TCP standard in Figure 3.3 is not predictive of the data for the other samples, failing to support the presence of a correctable determinate bias in the boats. (g) The correlation between the first and second sets of sample D is poor, again failing to support (see note f) that there is a correctable, determinate bias in the boats, but suggesting instead that the variation is an artefact of the samples or subsampling (see text for more discussion).

Precision is naturally poorer nearer to the detection limit (i.e., signal < 4), and MDE oil sample D was in this area. Thus, it is important not to place too much emphasis on the variation shown in Figure 3.3 or the poor correlations from sample D to D. Nevertheless, it is odd that the replicates of the same subsample in the same boat are so close to one another and replicates using a new subsample are so close to one another, but that the two means are so far apart, suggesting the subsamples are unlike. The samples tested were all below the region of interest (i.e., signal < 9), where sensitivity is not so important. This makes it more difficult to place the blame on the imprecision near the detection limit. A more thorough investigation would require F100 engine oil samples that span and exceed the region of interest, but these appear to have been generally unavailable in the past as well as now.

4. Recommendations and Conclusions

4.1. Measured Quantities and Dimensions (Units)

The switch from the arbitrary COBRA conductivity unit to the SI unit $\mu S\ cm^{-1}$ (or something very similar) should be done to improve traceability and accuracy. At the very least, a scale relating the COBRA measurement to an accepted traceable physical quantity should be developed to enable third-party external calibration and to ensure instrument performance. Furthermore, it has never been clearly stated whether the COBRA score should be framed in terms of a conductivity (reciprocal of resistivity), which is a property of the fluid itself, or a conductance (reciprocal of resistance), which combines the properties of the fluid and the properties of the cell in the measurement. The nature of the calibration suggests a conductivity, but does not require it. The lack of specifications or tolerances on the measurement sensor substantially contributes to the lack of specificity.

4.2. Boat Equivalence on the TCT

A more rigorous process must be established with more rigorous acceptance criteria for the TCT conductivity cell boats. A standardization process—either mechanical or algorithmic—must be instituted to correct for the biases shown in Figure 3.3 and the poor correlations in Table 3.5. The differences shown in Figure 3.3 are too high when the boat changes for the homogeneous TCP-in-TMPTH standard. Even if the artefactual influence of sampling speculated above accounts for the differences observed for the MDE oil samples, a difference of nearly 3 suggests that there is something intrinsically different about the boats. The high run-to-run repeatability on the same boat further supports this premise. However, any sort of software-based correction would require additional data obtained via multiple standards, which do not exist at present.

4.3. Expansion of the Calibration Region and Number of Calibration Points

One of the advantages of the TCT is that it is software-controlled and can readily accept multiple calibration points. The expansion to a four-point or five-point calibration curve that spans the region of interest would improve data quality significantly. The COBRA 2 does not have this feature.

4.4. Equivalence of COBRA 1, COBRA 2, and TCT

Acceptance of the COBRA II was predicated substantially upon repeatability and reproducibility on 9 instruments (*5*). Testing was conducted with three laboratory-formulated homogeneous solutions made by spiking TMPTH with an ionizable organic modifier. Differences of up to 2 units in the treated data were considered acceptable. Given the propagated error and the previous criteria, differences that are rounded to the nearest whole number and remain under 2.5 cannot be considered significant. Based on the data in this report, it is not possible to state conclusively that there is a difference among the COBRA 1, COBRA 2, and TCT. Such differences could only be determined by further testing on more instruments, but additional instruments were not available to us. The only unresolved issue is the equivalence of boats, but that could be addressed through a standardization process where sets of boats were verified to give equivalent signals over a range of conductivity standards.

5. References

(1) Toms, A. M.; Humphrey, G. R.; Squalls, M. S. *A Study on Instrumentation Methods Available for the Early Detection of #5 Bearing "Black Oil" and Other Degraded Oil Problems in F100-PW-100/200/220/229 Engines*. Joint Oil Analysis Program Technical Support Center, Pensacola, FL; March 10, 1995; Report No. JOAP-TSC-TR-95-03.

(2) Wright, R. L., Jr. *COBRA II Correlation Study and Field Performance Summary*. Wright Laboratory, Air Force Materiel Command; Wright-Patterson AFB, OH; November 1997; Report No. WL-TR-97-2097.

(3) Wyman, J.; Pitzer, E.; Williams, F.; Rivera, J.; Durkin, A.; Gehringer, J.; Serve, P.; von Minden, D.; Macys, D. Evaluation of shipboard formation of a neurotoxicant (trimethylol-propane phosphate) from thermal decomposition of synthetic aircraft engine lubricant. *American Industrial Hygiene Association Journal*; October 1993; 54 (10); 584-592.

(4) Centers, P.W.; Smith, F.D. *Real Time Simultaneous In-Line Wear and Lubricant Condition Monitoring*. Air Force Wright Aeronautical Laboratories, Air Force Systems Command; Wright-Patterson AFB, OH; June 1987; Report No. AFWAL-TR-87-2015; and references therein.

(5) Toms, A. M.; Rizzo, C.; Humphrey, G. R.; Lang, A. *A Study on Instrumentation Techniques Available for the Early Detection of "Burnt Oil" in F100-PW-100/200/220/229 Engines, Part II*. Joint Oil Analysis Program Technical Support Center, Pensacola, FL; February 18, 1997; Report No. JOAP-TSC-TR-97-01.

(6) JOAP Manual, volume 3, 2006, pages A-72–A-73; NAVAIR 17-15-50.3, TM 38-301-3, T.O. 33-1-37-3, CGTO 33-1-37-3.

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